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(54) **Hard steel sheet manufactured from aluminium-killed continuous-cast carbon-manganese steel, and a method for the manufacture of such sheet.**

(57) Steel sheet manufactured from Al-killed continuous cast carbon-manganese steel and having a hardness in the range 57 to 73 HR30T is characterized by a content of 0.03 to 0.10% by weight C and 0.15 to 0.50% by weight Mn, and an amount Z in ppm of dissolved uncombined nitrogen given by

$$Z \geq 2.5 \times (H-55)$$

where H is the hardness (HR30T). In this way, hard sheet is obtained at low Mn and C contents. In manufacture of the sheet, the thickness reduction in skin-passing is dependent on the uncombined nitrogencontent and an aging by heat treatment is performed after skin-passing.

EP 0 216 399 A1

OK
mention
temp of thermal treatment after skin-passing?

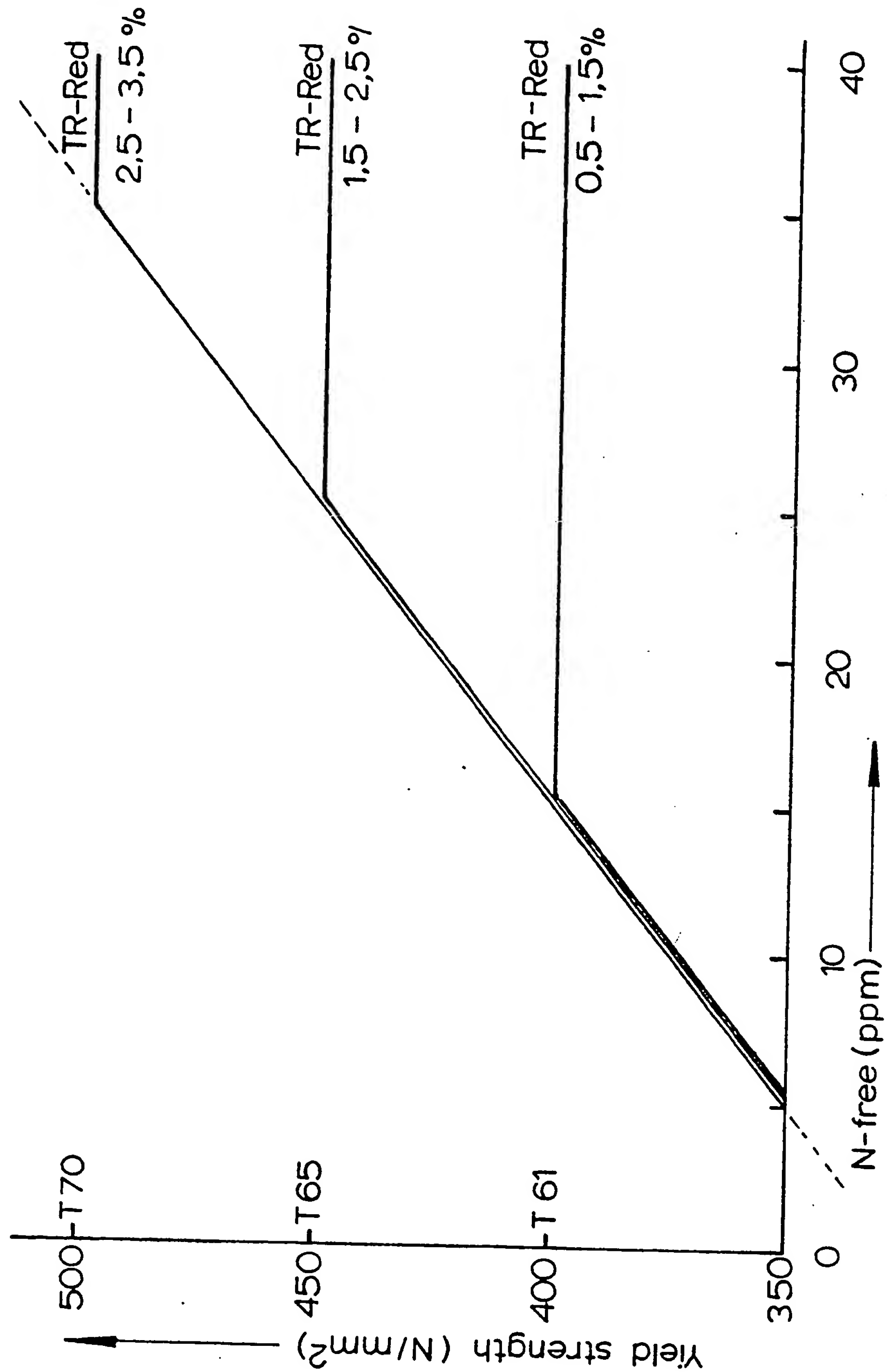
Yield strength (N/mm²)
500-T70
450-T65
400-T61
350
0
10
20
30
40
N-free (ppm)
TR-Red
2,5 - 3,5 %
TR-Red
1,5 - 2,5 %
TR-Red
0,5 - 1,5%

fig. 1

HARD STEEL SHEET MANUFACTURED FROM AL-KILLED CONTINUOUS-CAST CARBON-MANGANESE STEEL, AND A METHOD FOR THE MANUFACTURE OF SUCH SHEET.

The invention relates to hard steel sheet manufactured from Al-killed continuous cast carbon-manganese steel. The invention also relates to a method for manufacturing such sheet, including the steps of continuously casting the steel, hot-rolling, cold-rolling, continuously annealing and skin-passing (cold finishing).

In this specification and claims, by the term steel sheet is meant a product which has been hot-rolled, cold-rolled, annealed and skin-passed and which has a thickness of 0.1 to 0.5 mm. Such a sheet may additionally be provided with a metallic surface-layer such as for example tin or chrome/chromic oxide (ECCS) or with a chemical surface layer such as lacquer. Steel sheet is obtainable in various hardness categories. The softer qualities of sheet are used when, in manufacturing a product therefrom, the deformation given to the sheet is large, for example in the manufactur of certain cans. The harder qualities of sheet find use when the deformation to which the sheet is subjected is less large and strength requirements are set, such as for example with can ends.

The present invention aims for example particularly at the production of sheet in the hardness categories T61, T65 and T70 of European Standard 145-78 which is sheet with a hardness HR30T of 57 and higher. The mean hardness HR30T and the range permitted in these categories are as follows:

Hardness category	Hardness HR30T	
	Mean	Range
T61	61	±4
T65	65	±4
T70	70	+3 -4

HR30T is the Rockwell hardness using the 30T Rockwell Scale.

In other Standards, such as Tin Mill Products May, 1979 of AISI (American Iron and Steel Institute) and JISG 3303 (1984) of the Japanese Institute of Standards, other hardness-category designations are given, and there are slight deviations from the ranges of European 145-78 specified above. However grades of sheet defined in such other standards are deemed to satisfy European Standard 145-78 when the mean hardness-value HR30T corresponds to one of the categories T61,T65 and T70, and the present invention extends to these corresponding grades.

There are two known methods of producing hard qualities of sheet. The first method consists in that by skin-passing a great reduction of the thickness up to 15% of the thickness before skin-passing is obtained, the material being strengthened thereby. This has not only the disadvantage that a severe skin-passing is required but also that after skin-passing the steel sheet is more anisotropic, due to variations of mechanical properti s between the direction of rolling and the direction at right angles thereto, than is the case when in the skin-passing a smaller reduction in thickness is performed. This anisotropy can be serious when the steel is subsequently subjected to, for instance, deep-drawing or pressing.

The second known method consists in that a higher carbon and manganese content is used in the chemical composition of the steel than for the softer steel qualities. This makes the steel sheet harder and stronger, but a disadvantage is that steel with a higher carbon and manganese content is more expensive and offers great resistance to deformation during cold-rolling and skin-passing. Yet another disadvantage is that different chemical compositions are needed for different hardness categories, so that a manufacturer cannot start from a standard steel suitable for a range of qualities.

The object of the invention is to provide a hard-quality steel sheet and a m thod for manufacturing such sheet, in which the disadvantages r ferred to above are wholly or partly overcome.

The steel sheet according to th invention has the following characteristics, in combination:

a) the steel of the sheet contains, in percentage by weight, 0.03% to 0.10% carbon and 0.15% to 0.50% manganese, and

b) the steel of the sheet contains an amount of uncombined dissolved nitrogen (N_{free}) which for the respective hardness categories is given by the following table:-

Hardness category	N_{free} (ppm)
T61	$\geq$ 5
T65	$\geq$ 15
T70	$\geq$ 25.

The steel sheet according to the invention thus has a chemical composition which, as regards carbon and manganese content, can correspond to that usual in soft steels. It further has a particular minimum content of free nitrogen, which is not chemically combined, and is dissolved in the steel, which is achieved by control of the aluminium/nitrogen system. This nitrogen content -(N_{free}) can be directly determined and is equal or nearly equal to the difference between (a) the total quantity of nitrogen in the steel and (b) the quantity combined and precipitated in the form of A1N or other nitrides of aluminium or other nitrogen-binders.

A suitable maximum value of N_{free} is 100 ppm.

The invention can be defined without reference to European Standard 145-78 by relating the N_{free} value to the hardness. In this aspect the invention provides steel sheet manufactured from Al-killed continuous cast carbon-manganese steel and having a hardness in the range 57 to 73 HR30T characterized in that

(a) the steel of the sheet contains 0.03 to 0.10% by weight C and 0.15 to 0.50% by weight Mn, and

(b) the steel of the sheet contains an amount Z in ppm of dissolved uncombined nitrogen given by

$$Z \geq 2.5 \times (H-55)$$

where H is the hardness of the sheet (HR30T).

Preferably, the chemical composition of the steel comprises $\leq$ 0.065% acid-soluble aluminium Al_{as}(as = acid-soluble) and 0.004% to 0.010% N. This preferred upper limit of aluminium-content arises because the solubility of the nitrogen in the steel decreases with increasing aluminium-content. The lower limit of the nitrogen-content is dependent on the desired amount of free nitrogen N_{free} in the steel sheet, and the upper limit is determined by its suitability to cold-rolling. In addition, the chemical composition of the steel comprises for example max. 0.020 P, max. 0.020 S, max. 0.030 Si, the remainder being iron and the usual impurities.

Preferably therefore, the steel of the sheet of the invention has the composition, in % by weight:-

C	0.03	-	0.10
Mn	0.15	-	0.50
Al_{as} (acid soluble Al)	0	-	0.065
N (including said dissolved uncombined nitrogen)	0.004	-	0.010
P	0	-	0.02
S	0	-	0.02
Si	0	-	0.03

remainder Fe and inevitable impurities.

The steel sheet according to the invention is further characterized by a high yield-strength, which for the mentioned hardness-categories of European Standard 145-78 lies within the following limits:

Hardness category	Yield strength (N/mm^2)
T61	400 $\pm$ 50
T65	450 $\pm$ 50
T70	500 $\pm$ 50

The steel sheet of the invention can alternatively be defined by relating the N_{free} value to the yield strength. In this aspect, the invention provides steel sheet manufactured from Al-killed continuous cast carbon-manganese steel and having a hardness in the range 57 to 73 HR30T characterized in that

(a) the steel of the sheet contains 0.03 to 0.10% by weight C and 0.15 to 0.50% by weight Mn, and

(b) the steel of the sheet has a yield strength Y (N/mm^2) in the range 350 to 550 and contains an amount Z in ppm of dissolved uncombined nitrogen given by

$Z \geq 0.2 \times (Y-325)$.

A method of manufacturing the steel sheet according to the invention comprising the steps of continuous casting of the steel and hot-rolling, cold-rolling, continuous annealing and skin-passing is characterised in that, in combination:

a) the reduction in thickness TR-RED during skin-passing, expressed as a percentage, lies for the respective hardness-categories of European Standard 145-78 in the respective ranges:

Hardness category	TR-RED
T61	0.5 - 1.5
T65	1.5 - 2.5
T70	2.5 - 3.5

b) after the skin-passing, the steel is aged by a thermal after-treatment in which by fixing (saturating) free dislocations with free nitrogen, both the hardness and the yield strength are increased.

The method of the invention is alternatively characterized in that

a) the thickness reduction TR-RED (in %) during the skin-passing step is given by

$$\frac{H}{5} -11.5 \leq (\text{TR-RED}) \leq \frac{H}{5} -10.5$$

where H is the final hardness of the sheet (HR30T) with the proviso that TR-RED ≥ 0.5, and

b) after the skin-passing step a thermal - (heat) after-treatment is carried out in which free dislocations produced in the steel by the skin-passing are fixed by the uncombined nitrogen, so as to increase the hardness and yield-strength above the values after the skin passing.

The thermal after-treatment in the method of the invention achieves the aging of the steel by fixing, in the free dislocations created in the sheet by skin-passing, the free uncombined nitrogen dissolved in the steel. This thermal after-treatment may be combined with any other suitable thermal treatment of the skin-passed steel, e.g., a thermal treatment already known for another purpose.

For example, the steel sheet is tinned electrolytically after the skin-passing and the thermal after-treatment consists of fusing the tin-layer of the tinplate which has been deposited electrolytically. A second possibility is that the steel sheet is lacquered after skin-passing and the thermal after-treatment is to enamel the lacquer-layer of the lacquered sheet. The thermal after-treatments applied in these two embodiments, consisting of the fusing of the tin-layer or the enamelling of the lacquer layer, respectively, are apparently sufficient to bring about saturation of the free dislocations with free nitrogen.

Preferably, the coiling temperature of the sheet in the hot-rolling is less than 600°C, since in this case the free nitrogen remains largely in solution rather than having been converted into aluminium nitride as the coil cools. Further, in this way uniform distribution of free nitrogen over the whole length of the coil is achieved.

Figure 1 in the attached drawing is a graph showing the relationship in the practice of this invention between the yield strength and N_{free} at various values of thickness reduction TR-RED.

The method of the invention is exemplified by the functional relationship, illustrated in Figure 1, between the quantity of free nitrogen N_{free} present after the continuous annealing, the reduction in thickness TR-RED in the skin-passing and the resulting hardness and yield-strength conferred by the thermal after-treatment which follows the skin-passing step. With a thickness reduction in the range of 0.5% to 1.5% (i.e. a 1% level of thickn ss reduction) a nardness is obtained that increases with increase in the quantity of free nitrogen N_{free} present, when the quantity of free nitrogen N_{free} is less than 15 ppm. When the quantity of free nitrogen N_{free} exceeds 15 ppm, the hardness does not increase further. For a quantity of free nitrogen N_{free} greater than 15 ppm hardness-category T61 is thus produced with a reduction at the 1% level. Figure 1 also shows that for a quantity of free nitrogen N_{free} in excess, for example, of 35 ppm, steel sheet in the hardness-categories T61,T65 and T70 can all be achieved starting from one and the same steel, by employing appropriate thickness-reductions during cold-finishing (skin-passing). That is to say, for the same steel at 35 ppm N_{free}, TR-RED of 1% gives a steel sheet of category T61, TR-RED of 2% gives a steel sheet of category T65 and TR-RED of 3% gives a steel sheet of category T70.

EXAMPLE

A preferred embodiment of the invention is now described as a non-limitative example. The results here given are for a series of heats (steel compositions) carried out according to normal production processes. Each heat had a composition defined by the ranges (% by weight)

C	0.03	-	0.10
Mn	0.15	-	0.50
Al_{as} (acid soluble Al)	0	-	0.065
N (including said dissolved uncombined nitrogen)	0.004	-	0.010
P	0	-	0.02
S	0	-	0.02
Si	0	-	0.03

remainder Fe and inevitable impurities.

Each heat was continuously cast and the steel then hot-rolled with a coiling temperature of less than 600°C. The steel was cold-rolled into sheet with a cold-rolling reduction of 85-90%. The sheet was continuously annealed at above 640°C to obtain recrystallisation in a Mohri cycle. The sheet was then skin-passed with a skin-pass reduction of about 0.8%, and thereafter electrolytically tinned. A heat treatment to fuse the tin layer was finally performed, which also caused aging of the steel. The temper class (hardness class) and yield strength obtained in each case showed dependency on the uncombined nitrogen content (N_{free}) in accordance with the line for TR-RED of 0.5 - 1.5% in Figure 1.

There are many advantages of the sheet according to the invention and the method for manufacturing it. First, because of the low carbon and manganese contents, the steel has a "light" composition, so that the sheet is easier to roll than heavier compositions, since the hamdess is obtained by the thermal after-treatment. The "light" composition is also cheaper. In addition, the steel sheet is isotropic as a result of the small thickness-reduction in skin-passing. Lastly, steel of a single composition, provided the quantity of free nitrogen N_{free} present is high enough, can suffice to produce different hardness-categories, by skin-passing with appropriate small reductions in skin-passing.

Claims

1. Steel sheet manufactured from Al-killed continuous cast carbon-manganese steel and having a hardness in one of the hardness categories T61, T65 and T70 of European Standard 145-78 characterized in that

(a) the steel of the sheet contains 0.03 to 0.10% by weight C and 0.15 to 0.50% by weight Mn, and

(b) the steel of the sheet contains an amount of uncombined dissolved nitrogen (N_{free}) which for the respective hardness categories is given by the following table:-

Hardness category	N_{free} (ppm)
T61	$\geq$ 5
T65	$\geq$ 15
T70	$\geq$ 25.

2. Steel sheet according to claim 1 which contains ≥ 0.065% by weight acid-soluble Al and 0.004 to 0.010% N.

3. Steel sheet according to claim 1 or claim 2 wherein the yield strength of the steel of the sheet is given, for the respective hardness categories, by the following table:-

Hardness category	Yield strength (N/mm^2)
T61	400 ± 50
T65	450 ± 50
T70	500 ± 50.

4. Steel sheet manufactured from Al-killed continuous cast carbon-manganese steel and having a hardness in the range 57 to 73 HR30T characterized in that

(a) the steel of the sheet contains 0.03 to 0.10% by weight C and 0.15 to 0.50% by weight Mn, and

(b) the steel of the sheet contains an amount Z in ppm of dissolved uncombined nitrogen given by

$Z \geq 2.5 \times (H-55)$

where H is the hardness of the sheet (HR30T).

5. Steel sheet manufactured from Al-killed continuous cast carbon-manganese steel and having a hardness in the range 57 to 73 HR30T characterized in that

(a) the steel of the sheet contains 0.03 to 0.10% by weight C and 0.15 to 0.50% by weight Mn, and

(b) the steel of the sheet has a yield strength Y (N/mm^2) in the range 350 to 550 and contains an amount Z in ppm of dissolved uncombined nitrogen given by

$Z \geq 0.2 \times (Y-325)$.

6. Steel sheet according to claim 4 or claim 5 having the composition, in % by weight:-

C	0.03	-	0.10
Mn	0.15	-	0.50
Al_{as} (acid soluble Al)	0	-	0.065
N (including said dissolved uncombined nitrogen)	0.004	-	0.010
P	0	-	0.02
S	0	-	0.02
Si	0	-	0.03

remainder Fe and inevitable impurities.

7. Method of manufactuing steel sheet according to any one of claims 1 to 3 including the steps of

i) continuously casting the steel

ii) hot-rolling the steel

iii) cold-rolling the steel

iv) continuously annealing the steel

v) skin-passing the steel

characterized in that

a) the thickness reduction TR-RED (in %) during said skin-passing step is, for the respective hardness categories, within the ranges given by the following table:-

Hardness category	TR-RED (%)
T61	0.5 - 1.5
T65	1.5 - 2.5
T70	2.5 - 3.5

b) after the skin-passing step a thermal - (heat) after-treatment is carried out in which free dislocations produced in the steel by the skin-passing are fixed by the uncombined nitrogen, so as to increase the hardness and yield-strength above the values after the skin passing.

8. A method according to claim 7 wherein the steel sheet is tinned electrolytically after the skin-passing and the said thermal after-treatment consists of the fusing of the electrolytically-deposited tin layer.

9. A method according to claim 7 wherein the steel sheet is lacquered after the skin-passing and the said thermal after-treatment consists of the enamelling of the layer of lacquer.

10. A method according to any one of claims 7 to 9 wherein the coiling temperature at hot-rolling is less then 600°C.

11. Method of manufacturing steel sheet according to any one of claims 4 to 6 including the steps of

(i) continuously casting the steel

ii) hot-rolling the steel

iii) cold-rolling the steel

iv) continuously annealing the steel

v) skin-passing the steel

characterized in that

a) the thickness reduction TR-RED (in %) during the skin-passing step is given by

$$\frac{H}{5} - 11.5 \leq (\text{TR-RED}) \leq \frac{H}{5} - 10.5$$

where H is the final hardness of the sheet (HR30T) with the proviso that TR-RED ≥ 0.5, and

b) after the skin-passing step a thermal - (heat) after-treatment is carried out in which free dislocations produced in the steel by the skin-passing are fixed by the uncombined nitrogen, so as to increase the hardness and yield-strength above the values after skin passing.

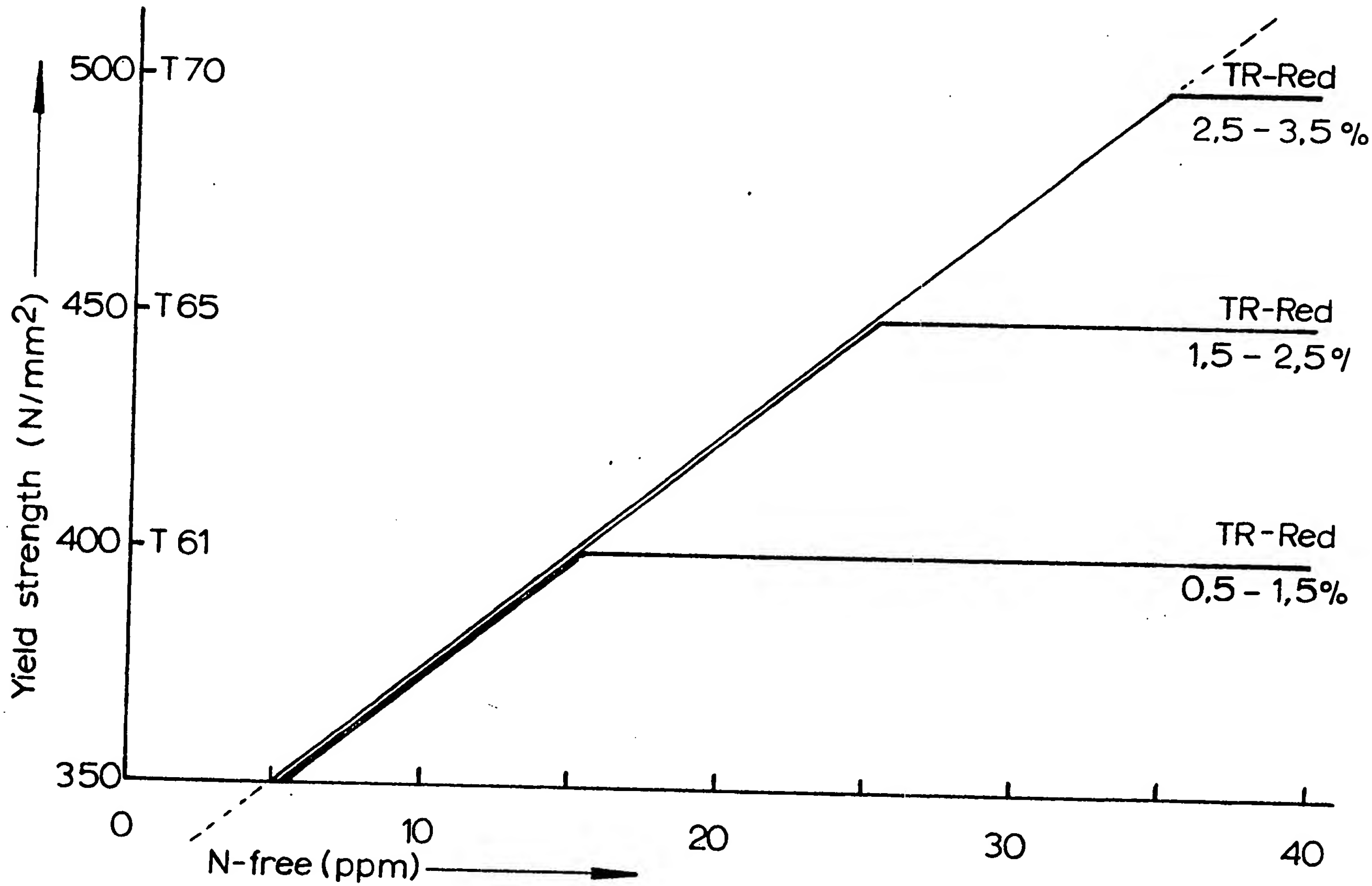
TR-Red
2,5 - 3,5 %
TR-Red
1,5 - 2,5 %
TR-Red
0,5 - 1,5%
500-T70
450-T65
400-T 61
350
0
10
20
30
40
N-free (ppm)
Yield strength (N/mm²)

fig. 1

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 20 1214

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB-A-1 464 232 (NIPPON KOKAN K.K.) * Claim 1; page 1, lines 12-32; page 4, line 19 - page 5, line 20 *	1,2,4	C 22 C 38/00 C 21 D 8/02 C 25 D 3/30 C 25 D 5/50

A	FR-A-2 166 064 (NIPPON STEEL CORP.) * Claim 1; page 10, table I; examples B,C,F *	1,2	

A	FR-A-2 013 931 (NIPPON KOKAN K.K.) * Claim 1 *	1,2	

A	FR-A-2 012 107 (NIPPON KOKAN K.K.) * Claims 1,2; page 1, lines 25-28 *	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 22 C 38 C 21 D C 25 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20-11-1986	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the applicati n
L : document cited for other reasons

& : member of the same patent family, corresponding document